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Development of Hot Melt Flexible Polyimide Sealants for Rapid Sealing of Aircraft and Missiles

Final Technical Report

Contract No. N62269-82-C-0732

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<p>Studies were conducted on a baseline hot-melt flexible polyimide formulation developed on a previous NADC contract for potential application as a quick-fix field repair sealant for Navy aircraft and missiles. The baseline formulation was 1.0:0.5:0.6 by mol methylenedianiline (MDA):bismaleimidophenylmethane (BMPM):Jeffamine ED-900 bismaleimide (BMJ[900]).</p> <p>Studies consisted of Task I - Flexible Polyimide Optimization & Scale-up - and Task II - Resin Compounding & Hot Melt Tool Development - and III - Finalize Sealant Evaluation Studies. Different variations of filled and compounded formulations were prepared and examined for solvent, water immersion, and humidity stability. Efforts were conducted to prepare a formulation suitable for extrusion through a commercially available hot-melt sealant applicator. No one resin was found to meet the program goal requirements. Because of this, Task IV - Field Demonstration - was not performed, with concurrence of the NADC Technical Monitor.</p>					
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FOREWORD

This Final Report describes work performed by TRW Electronics and Defense Sector during the period 11 September 1982 to 30 June 1984 on Contract N62269-82-C-0732, Development of Hot Melt Flexible Polyimide Sealants for Rapid Sealing of Aircraft and Missiles, sponsored by the Naval Air Development Center (NADC), Warminster, Pennsylvania. Coleman Nadler served as the NADC technical monitor.

The TRW Program Manager was G. E. C. Chang. Technical support was provided by T. W. May, W. F. Wright, and K. Yates. Administrative review was provided by R. J. Jones, Business Area Manager, Chemical Technology Operations, and B. Dubrow, Manager, Chemical Technology Operations.

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SECTION I. INTRODUCTION

An important need exists for a versatile field-repair sealant for operational aircraft possessing key application/cure properties to enable rapid sealing against water intrusion and corrosion, to maintain pressurized areas and fuel vapor barriers, and for similar measures under normal fleet operations. In the field, conditions could range from a cool day of, say, 40°F to temperatures over 100°F, while relative humidities could reach 95% or higher. An ideal candidate should be readily applicable, yet rapidly curable enough so that typical turnaround time is less than 4 hours. The most appropriate seems to be a practically instantaneous-curing, one-component material that can be applied in hot-melt fluid form with a hand-held tool for these gap, seam, and fillet type sealing operations.

TRW Electronics and Defense Sector has been working since the late 1960's on innovative approaches to sealant development for military applications. In particular, a TRW-developed hot-melt processable material called the flexible polyimide resins was developed and successfully demonstrated as a sealant/adhesive fed through a TRW-designed applicator tool.

In 1981, TRW was awarded Contract N62269-81-C-0738 by Naval Air Development Center (NADC), Warminster, Pennsylvania, to investigate the hot-melt-processable flexible polyimide technology as a means to develop a versatile, rapid-curing structural sealant for field repair of Navy aircraft. The efforts entailed formulation studies of neat resin systems with *in situ* crosslink capabilities, and involved optimization of these key sealant properties: work time, tensile strength and elongation, adhesion, low temperature flexibility, cold/hot flow, fluid resistance, and storage stability. Two neat resin formulations showed promise in fulfilling the requirements of a rapid-curing field-repair sealant for Navy aircraft in each of the key properties listed above. As a result, TRW recommended further study to optimize the performance of these two neat resin formulations.

In 1982, TRW was awarded Contract N62269-82-C-0732 for this very purpose: to continue optimization studies on these two promising neat

resin formulations to maximize performance in regard to the aforementioned property requirements and to develop one most promising system for quick-fix field repair of Navy aircraft. This twelve-month study involved four tasks:

Task I - Flexible Polyimide Resin Optimization and Scale-Up

Task II - Resin Compounding and Tool Development

Task III - Finalized Sealant Evaluation Studies

Task IV - Field Demonstration

The details of the results, and the discussions and recommendations thereof, constitute the remainder of this Final Report on NADC Contract N62269-82-C-0732.

SECTION II. TECHNICAL DISCUSSION

The work described herein was an optimization of the properties of the two most promising neat resin formulations discovered on NADC Contract N62269-81-C-0738. The objective was to develop TRW's flexible polyimides as a rapidly-curing hot-melt field-repair sealant/applicator system for Navy aircraft, where unclean surfaces, temperature extremes, and fuel, hydraulic fluid, water and cleaning compound exposure exist. These studies included: investigations of chair extenders/cure promoters, adhesion promoter additives, surface primers, and other formulations (Task I); compounding with fillers and/or reactive diluents and hot-melt tool development (Task II); finalized sealant exposure studies to aircraft fuel, MIL-L-23699 oil, heat, and water/vapor at elevated temperatures (Task III); and a field demonstration of the most promising sealant/applicator system (Task IV).

A brief background summary follows.

Background

A decade ago TRW developed a novel class of resins, designated compliant or flexible polyimides, under a United States Air Force sealant development program. These were linear condensation polyimides consisting of aromatic and flexible aliphatic ether segments linked by imide units. Through a progression of innovations, these were modified to include 1) unsaturation

sites suitable for crosslinking, 2) solventless systems, 3) addition polymerization as a mechanism for polymer preparation, and 4) hot-melt extrudability. (A more detailed background is given in Reference 1.)

The general chemical reaction scheme is shown in Equation 1. The Michael-type addition polymerization of the bismaleimide of methylene dianiline, or BMPM, and those of polyaliphatic ether diamines (the Jeffamine ED and less polar D series available from Texaco Jefferson Chemical Company), or BMJ's, in the presence of additional methylene dianiline (MDA), produced resins having high tensile and highly promising sealant properties over a range of varying stoichiometries of the three monomeric ingredients. These results provided the impetus for employing the flexible polyimide technology on NADC Contract N62269-81-C-0738.

The NADC-sponsored program investigated twenty formulations involving varying ratios of BMPM, BMJ's, and MDA. The ingredients and resin compositions are shown in Tables I and II. Two formulations were most promising in terms of toughness, flexibility, adhesion to aluminum, and stability upon exposure to heat, high humidity and fluid immersion (fuel, hydraulic fluid, cleaning solution, and water). A summary of representative properties is presented in Table III. Upon completion of this program, TRW recommended that these two resin formulations be studied further to maximize performance requirements for the aforementioned properties.

The results of the previous NADC-sponsored program led to the award to TRW of NADC Contract N62269-82-C-0732, which is the subject of this Final Report. The remainder of this Section describes the optimization effort conducted along the guidelines of the four tasks described earlier.

Task I: Flexible Polyimide Optimization and Scale-Up

This task was intended to optimize the two most promising resins from the previous program (Contract N62269-81-C-0738) in terms of maximum performance, relative to moisture, cleaning compound and aircraft fluid stability; high level and durable adhesion; rapid cure/crosslinking at 400°F or less; low-temperature (-65°F) flexibility; and stable physical properties (tensile and tear strength, elongation, storage stability, adhesion, etc.). Studies were to include investigations of chain

TABLE I. LEADING RAW MATERIAL CANDIDATES

Monomer Name *	Monomer Abbreviation	Monomer Structure
1. MALEIMIDES BIS (MALEIMIDES) OF JEFFAMINE ED SERIES • 600 MW • 900 MW • 2000 MW	BMJ (600) BMJ (900) BMJ (2000)	<p> $a + c = 3.5, b = 13.5$ $a + c = 3.5, b = 20.5$ $a + c = 3.5, b = 45.5$ </p>
BIS (MALEIMIDES) OF JEFFAMINE D SERIES • 400 MW	BMJ (D4)	<p>$a = 5.6$</p>
BIS (4-MALEIMIDO PHENYL) METHANE	BMPM	
2. AROMATIC AMINES METHYLENE DIANILINE	MDA	

*JEFFAMINE IS A REGISTERED TRADEMARK OF THE JEFFERSON CHEMICAL COMPANY.

TABLE II. HOT MELT PROCESSABLE POLYIMIDE FORMULATIONS

Ingredient	Formulation (Parts by mol)																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
MDA	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
BMPM	0.6	0.5	0.4	0.9	0.75	0.65	0.5	1.2	1.0	0.9	0.5	0.45	0.4	0.6	0.55	0.4	0.5	0.4	0.2	0.5
BMJ (600)	0.7	0.8	0.9	--	--	--	--	--	--	--	--	0.75	0.7	--	--	--	--	--	--	--
BMJ (900)	--	--	--	0.4	0.55	0.65	0.8	--	--	--	0.6	--	--	0.7	0.65	0.7	--	--	--	0.7
BMJ (2001)	--	--	--	--	--	--	--	0.1	0.3	0.4	--	--	--	--	--	--	--	--	--	--
BMJ (D4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.7	0.8	1.0	--
Excess maleimide double-bond (cross-linkable site) functionality (%)	30	30	30	30	30	30	30	30	30	30	10	20	10	30	20	10	20	20	20	20

TABLE III. MOISTURE AND FLUID IMMERSION STABILITY OF HOT MELT PROCESSABLE POLYIMIDE FORMULATIONS.

Formulation ^{a)} from Table IV	JP-5 Fuel	MIL-H-83282 Fluid	Deionized Water	MIL-C-43616 Fluid
1	Excellent	Excellent	Good adhesion and stability up to 3 days immersion (60 min./400°F cure)	Good adhesion and stability up to 3 days immersion (60 min./400°F cure)
2	Excellent	Excellent	Fair-good adhesion, 5-7 days; embrittlement and swell, 5-7 days (60 min./400°F cure)	Fair-good adhesion, 5-7 days; embrittlement and swell, 5-7 days (60 min./400°F cure)
7	Excellent	Excellent	Fair-good adhesion up to 2 days; embrittlement and swell after 2 days (60 min./ 400°F cure)	Fair-good adhesion up to 2 days; embrittlement and swell after 2 days (60 min./400°F cure)
11	Excellent	Excellent	Adhesion up to 5 days; some embrittlement after 5 days (60 min./400°F cure)	Adhesion up to 5 days; some embrittlement after 5 days (60 min./400°F cure)
14	Excellent	Excellent	Good adhesion up to 5 days; embrittlement and swell after 5 days (10 min./350°F cure)	Good adhesion up to 5 days; embrittlement and swell after 5 days (10 min./350°F cure)

a) Formulations 3, 9, 10, 12, 13 and 20 were very tacky after cure and deemed unsatisfactory for immersion tests; conversely, formulations 4, 5, 6, 8, 15, 16, 17, 18 and 19 were very brittle after cure with little or no adhesive strength and also deemed unsatisfactory for test.

extenders/cure promoters such as divinyl benzene, peroxide cure catalysts and adhesion promoter additives, e.g., functional silanes, blocked reactive resins, and surface primers. Table IV shows the formulary ingredients initially proposed to be studied, along with a brief explanation of predicted effect on properties.

In the course of this task, the decision was made in conjunction with the NADC engineer to concentrate on one resin formulation from the previous program: that comprised of MDA:BMPM:BMJ(900) in 1.0:0.5:0.6 molar ratio (see Table I for compound structures). This decision was based on the superior properties and performance in environmental aging tests (see Table III. This formulation will hereafter be referred to as the baseline resin.

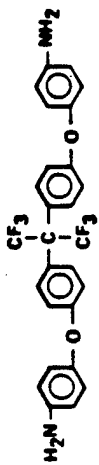
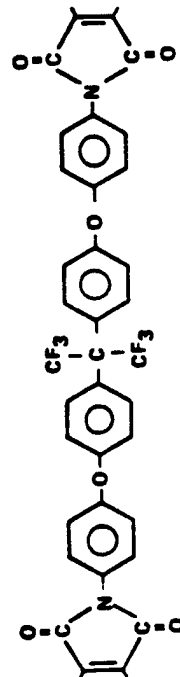
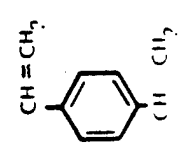
Another decision was made to initiate part of Task II in parallel with Task I. This part of Task II is described below.

Task II (in part) - Resin Compounding

This part of Task II was intended to subject neat resin to compounding with fillers and thixotropic agents (e.g., Cab-O-Sil and other fused silicas, aluminum, clays, etc.), and with reactive diluents and/or plasticizers (e.g., diallyl phthalate and other rheology-control additives) to achieve reasonable work time (>1 minute) and melt viscosity (estimated 1000 poises or lower) at elevated temperature (initially 149°C or 300°F) and to form non-porous seals with minimal drip or flow on vertical and overhead surfaces. The similarity of this part of Task II with the practice of Task I prompted a combined systematic resin modification/compounding study to determine the proper combination of these cure/adhesion promoters, fillers, reactive diluents, and plasticizers to achieve elevated-temperature melt-flow characteristics as well as desired sealant properties at $T \leq 120^\circ\text{C}$ (250°F). With concurrence of the NADC engineer, this proposed study was accepted.

Initial efforts involved the addition of Cab-O-Sil M-5 to our baseline resin [1.0:0.5:0.6 MDA:BMPM:BMJ(900)]. MDA and BMJ(900) were mixed together for 50 minutes while temperature rose to 100°C (212°F), then BMPM and Cab-O-Sil were added together and temperature increased to 120°C (250°F)


TABLE IV
FORMULARY INGREDIENTS PROPOSED FOR STUDY

Name/ Abbreviation	Structure	Purpose
2,2-Bis[4-(4-aminophenoxy)- phenyl]hexafluoropropane 4-BDAF		This four ring diamine, when substituted in whole or part for methylene dianiline, may offer improved resin tensile flexibility and moisture resistance due to fewer imide linkage/unit molecular weight. It is currently available to TRW in developmental quantities under license to Morton Chemical Company.
Bis(maleimide) of 4-BDAF		This compound, when substituted in whole or part for the bis(maleimide) of methylene dianiline, in conjunction with 4-BDAF and/or MDA, may offer additional property improvements to those stated above.
Divinyl Benzene DVB		This compound, when employed as a curing agent, may offer improved crosslinking of cured sealants. Peroxide catalysts such as Lupersol 130 will be investigated in conjunction with DVB.

(Continued)

TABLE IV (continued)

FORMULARY INGREDIENTS PROPOSED FOR STUDY

Name/ Abbreviation	Structure	Purpose
Diaminostilbene DASB		This compound, when employed as a chain extender in conjunction with MDA or 4-BDAF will provide internal cure sites for cross-linking which may improve sealant swelling in moisture. It can also be used in conjunction with the DVB approach.
Bis(maleimide) mixture of Jeffamine D-400 and D-2000 [(BMJ(D4) and BMJ(D20), respectively]	$\text{H}_2\text{NCH}_2\text{CH}_2\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{O}-\text{CH}-\text{CH}_2 \end{array}\right)_x \text{O}-\text{CH}_2\text{CH}_2\text{NH}_2$ <p>where $x = 5$ and 32</p>	These compounds, containing less polarity, may offer improved sealant moisture resistance.

over 20-25 minutes, at which time the resin was viscous enough to begin "climbing" the overhead stirrer shaft. Samples of these filled resins on flexible aluminum were cured at 204°C (400°F) for 20 minutes and examined.

The effect of reactive diluents both on neat resin and on resin filled with various levels of incorporated Cab-O-Sil filler was also investigated. The reactive diluents were divinylbenzene and diallyl phthalate. The method of preparation was essentially the same as with Cab-O-Sil filler with either reactive diluent. A sample of each formulation was cured at 204°C (400°F) for 15 min, then examined for toughness, flexibility, and adhesion. Table V below summarizes the results of these initial resin modification studies.

TABLE V. BASELINE RESIN MODIFICATIONS^{a)}

Resin No.	Reactive Diluent (parts by mol)		Filler Cab-O-Sil, Wt %	Resin Quality (Cured) ^{b)}
	Divinylbenzene (DVB)	DiallylPhthalate (DAP)		
1	--	--	2	Little difference from unfilled resin
2	--	--	3	same
3	--	--	5	Too stiff for adequate melt/flow
4	0.1	--	3	Tacky, extensive cold-flow
5	0.05	--	5	Tough, flexible, good adhesion
6	0.1	--	5	Very tough, good adhesion; smooth surface, some internal voids
7	--	0.1	--	Fair-good adhesion; some voids; fairly tough
8	--	0.1	3	Spongy, voids; smooth surface; moderate adhesion.

^{a)} Baseline resin: 1.0:0.5:0.6MDA:BMPP:BMJ(900), parts by mol.

^{b)} Cure conditions: 204°C (400°F) in air, 15 min.

The presence of additional crosslinking agents seems to enhance toughness after cure, without apparent detriment to adhesion or flexibility. The drawback is the lack of dimensional stability in the uncured resin, and the stench of divinylbenzene, apparently a better reactive diluent than diallyl phthalate from these admittedly few data points.

As part of Task I, some modifications of the diamine component in the flexible polyimide formulation (see Equation 1) were explored. TRW's proprietary diamine, 4-BDAF (see Table II), was substituted for varying portions of MDA, both in filled and unfilled resin. The results are shown below.

RESIN MODIFICATIONS INCORPORATING 4-BDAF

Resin No.	Ingredient (parts by mol)						Cab-O-Sil Filler, wt %	Cured Resin Quality ^{a)}
	MDA	4-BDAF	BMPM	BMJ(900)	DVB	DAP		
9	0.8	0.2	0.5	0.6	--	--	--	Tough, rubbery; wrinkled surface, internal voids; very good adhesion.
10	0.8	0.2	0.5	0.6	--	--	3	Smooth surface, very small internal voids; very tough, rubbery, very good adhesion.
11	0.8	0.2	0.5	0.6	--	--	5	Tough, rubbery; irregular surface; small internal voids; good adhesion.
12	0.9	0.1	0.5	0.6	--	--	3	Tough, rubbery; very rough surface; small voids; good adhesion.
13	0.9	0.1	0.5	0.6	--	--	5	Tough, rubbery; very rough surface; small voids; good adhesion.
14	0.7	0.3	0.5	0.6	--	--	3	Tough, rubbery; slightly rough surface; small voids; good adhesion.
15	0.9	0.1	0.5	0.6	0.1	--	3	Tough, rubbery, small voids; good adhesion.
16	0.9	0.1	0.5	0.6	--	0.05	3	same

^{a)} Cure conditions: 15 min at 204°C (400°F) in air.

The results indicate that cured resins containing 4-BDAF seem to possess very similar properties at least up to 30 mol % of the diamine component. The presence of filler seems to cut down on voids content. As with previous formularies, 3% by weight seems to be an optimum loading of Cab-O-Sil filler, while at 5% (and presumably above) the resin begins to become too "stiff" even in uncured states to be manageable.

Of the 16 resin modifications examined so far, five looked most promising in terms of toughness, flexibility and adhesion to aluminum: resins 2, 3, 12, 15 and 16. At this point it was decided to subject these most promising modified resins to environmental screening. Triplicate samples on aluminum were cured at 204°C (400°F) for 15 minutes and immersed in JP-5 fuel, MIL-H-83282 hydraulic fluid, distilled water, and dilute (9:1 v:v) MIL-C-43616 cleaning fluid, at ambient temperature and 60°C (140°F), and examined for volume swell over a period of seven days.

All five candidates showed excellent resistance to JP-5 fuel and MIL-H-83282 hydraulic fluid; however, they all showed considerable swelling in both water and in dilute MIL-C-43616 cleaning solution, at room temperature and at 60°C (140°F), on the order of 100-150% by weight and volume even after 24 hours. However, many of the samples were of less than optimum quality: porous, with many voids, offering ample opportunity for entrainment of water. Indeed, when they were dried in an oven at 120°C (250°F) for half an hour, their weights and volumes decreased to near their original values, as seen before with these types of resins.

These results imply that formulary optimization has not worked any dramatic improvement in sealant properties to date—at least of those so far employed in Task I. The possibility exists that either a) a higher cross-linking density (e.g., greater divinylbenzene content), or b) incorporation of the more water-resistant flexibilizing segments in the polymer backbone (e.g., a mixture of Jeffamine D400 and D2000 bis-maleimides—see Table II) will show significant improvement in neat resin properties.

The real promise, though, may lie in compounding and filling studies. Dramatic changes in other types of polymers in terms of viscosity, rheological properties, and adhesion capabilities, have been seen when additives such as organic titanates and various fillers (coated silicas, clays, etc.) have been included in resin formulations. A systematic investigation of the effect of such compounding ingredients is a main activity of Task II.

In light of the previous results, the decision was made to terminate the activities of Task I and carry on two promising resin candidates into Task II—Resin Compounding and Hot Melt Tool Development. The reasons on which this decision is based are as follows: 1) the resin modifications as outlined in the previous reports have shown no dramatic improvement in resin performance, especially stability in water or dilute MIL-C-43616 cleaning compound; 2) the true promise of increased resin performance seems to lie in compounding, as outlined in the Statement of Work for Task II.

The two resins are shown below (ingredients shown as parts by mol):

<u>MDA</u>	<u>BMPM</u>	<u>BMJ (900)</u>	<u>BMJ (D4-D20)</u>
1.0	0.5	0.6	---
1.0	0.5	--	0.6

The ingredient, BMJ (D4-D20), is a mixture of the bismaleimides of the Jeffamines D-400 and D-2000 (see Table II). The Jeffamines were formulated to give an average molecular weight of 900, then converted to bismaleimides in a manner analogous to that employed for conversion of Jeffamine ED-900 to BMJ (900). The premise is that the lower polarity in the D-type structures will provide improved moisture resistance in the derived flexible polyimides over those incorporating BMJ (900).

These two resins were then formulated, as before, with different levels of filler (i.e., thixotropic agents) and reactive diluent (i.e., divinylbenzene). In addition, the first attempts at incorporation of organic titanate additives were made. These latter reagents have been shown to exert dramatic changes in adhesion and rheology characteristics in other polymer types.² In this case, incorporation of two to five parts per thousand of a suggested organic titanate, KR238J (available from

Kenrich Petrochemicals, Inc.), in either resin shown above greatly lowers the viscosity prior to cure, increases the adhesion capability of resin to 7075 aluminum substrate after cure, and eliminates most or all of the voids seen previously upon curing these resins.

A typical procedure is as follows: MDA and BMJ (900) [or BMJ (D4-420)] are stirred and heated in an oil-bath (bath temperature from ambient to 120-125°C over 40 min., then held there for another 30-40 min.). Then KR238J (five parts per thousand by weight) is added; the mixture is stirred another 2-5 min. Then BMPM, divinylbenzene, and other filler or fillers are added sequentially. The mixture is stirred another 10-20 min., then poured onto an aluminum substrate. Final cure is done in an air-circulating oven (350-450°F for 20-30 min.).

The use of divinylbenzene as a reactive diluent (i.e., a latent crosslinking agent) seems to add toughness to the resin. In the course of these studies, an optimum amount of divinylbenzene seems to be 20 mol percent. Whether this is sufficient, in conjunction with KR238J additives and filler content (see below), to impart maximum moisture resistance, remained to be seen when the immersion tests were completed.

Several different fillers have been employed so far: Cab-O-Sil M5, Hi-Sil EF, powdered Teflon, and Aerosil R972. The first two are silicas. Cab-O-Sil has an average particle size of 12 μm , and has a proprietary coating which enables it to be more easily "wetted" by resin. Both are reinforcing-type fillers, and impart a significant degree of stiffness to resin. Powdered Teflon was investigated as a hydrophobic filler which could possibly increase moisture resistance; it does, however, have a significant "wetting" problem with these resins, and seems to create voids. Aerosil R972 has comparable particle size to Cab-O-Sil, but is coated with a hydrophobic material, hence the reason for its investigation; it also is a reinforcing-type filler.

In addition, several formulations incorporating powdered aluminum were investigated. The intent in these cases was to employ an appropriate thixotrope, as well as making the resin more compatible with the aluminum substrate in terms of expansion and/or contraction and moisture resistance.

Shown below are the new formulations prepared to date based on the above two resins:

Resin No.	MDA ^{a)}	BMPM ^{a)}	BMJ(900) ^{a)}	BMJ(D4-D20) ^{a)}	DVB ^{a)}	KR238J ^{b)}	Hi-Sil ^{b)} EF	Teflon ^{b)}	Aerosil ^{b)} R972	Aluminum ^{b)}
17	1.0	0.5	0.6	--	0.2	0.5	5	--	--	--
18	1.0	0.5	0.6	--	0.2	0.5	--	5	--	--
19	1.0	0.5	0.6	--	0.2	0.5	--	--	5	--
20	1.0	0.5	0.6	--	0.2	0.5	--	--	5	5
21	1.0	0.5	--	0.6	0.2	0.5	5	--	--	--
22	1.0	0.5	--	0.6	0.2	0.5	--	5	5	--
23	1.0	0.5	--	0.6	0.2	0.5	--	--	--	--
24	1.0	0.5	--	0.6	0.2	0.5	--	--	--	5

a) Parts by mol

b) Weight percent.

These resins, on 7075 aluminum substrates, were cured at 350-400°F for 20-30 min., and then subjected to immersion in distilled water and in 9:1 v:v water : MIL-C-43616 cleaning compound at ambient temperature as a quick screening test. The results are shown below.

Resin No.	Volume Swell (%) in H ₂ O			Volume Swell (%) in MIL-C-43616		
	24 Hr	48 Hr	144 Hr	24 Hr	48 Hr	144 Hr
17	50 ^{a)}	--	--	50 ^{a)}	--	--
18	50 ^{a)}	--	--	50 ^{a)}	--	--
19	50 ^{a)}	--	--	50 ^{a)}	--	--
20	50 ^{a)}	--	--	50 ^{a)}	--	--
21	10	10	20	10	10	20
22	10	10	20	10	10	20
23	10	10	20	10	10	20
24	10	10	20	10	10	20

a) Test ended.

The BMJ (900) containing resins showed pronounced swell—greater than 50%—even after 24 hours, while the BMJ (D400-D2000) containing resins showed significantly lower swell. This is, however, mitigated by the fact that the 350-400°F cure—a simulation of a typical hot-melt applicator temperature at the point of extrusion—gives rise to voidy, rather spongy cured resin. The entrainment of fluids could then be made more facile, hence the enhanced volume swell in the BMJ (900) containing resins. The inherently greater resistance of the D-series maleimide-containing resins, despite a similar voids content problem, favors these as the resins of choice.

The cause of the voids may be from general sources: a) residual volatiles from the BMJ preparation, removed only at this high temperature; b) volatiles (i.e., water) from imidization of some non-imidized BMJ's which occurs at this high temperature; c) volatiles of some sort from the crosslinking of divinylbenzene or side-reactions thereof; d) volatiles from some high-temperature side-reaction in the polymer backbone. Point a) is least likely, since preparation of the BMJ's involves, as the final step, removal of volatiles *in vacuo* (at ca 1 mm Hg) at 85-90°C; however, a verification can be made by longer stripping of these BMJ's, and also by *in vacuo* treatment of prepared resin. Point b) may be likely, and can be eliminated by longer and more stringent imidization conditions in BMJ preparation. Point c) may be likely; however, this high-temperature voidiness during cure has been observed even without divinylbenzene present, as seen in earlier experiments and in the program previous to this present one. This implies a possibility that point d) may be occurring; this can be tested however, by the proposed conditions to eliminate points a), b), and c), and then conducting a brief temperature-reactivity study on prepared resin to deduce where the onset of this voidiness occurs.

A comment should be made at this point, though, that the lower-temperature cure—250°F for 2-8 hours—does eliminate the voids problem. Indeed, optimally-cured resin (at 250°F) does not develop voids when subsequently heated at 350-400°F for 30 minutes. This piece of promising data, however, must be reconciled with the fact that the uncured resin does not melt or flow properly until at least 350°F.

In order to test the resistance of optimally-cured, void-free resins to water and MIL-C-43616 compound, several more formulations were prepared on 7075 aluminum and cured at 250°F for 4 hours. The possibility of point c) was eliminated by leaving divinylbenzene out of the formulary. Teflon, Hi-Sil, and Aerosil R972 were also eliminated from the resins, and the only filler was aluminum powder, since it seemed to impart added stiffness and decreased swelling capability (as well as an interesting green color). The KR238J titanate additive was used in each case. The resins are shown below:

<u>Resin No.</u>	<u>MDA^{a)}</u>	<u>BMPPM^{a)}</u>	<u>BMJ(900)^{a)}</u>	<u>BMJ(D400-D2000)^{a)}</u>	<u>KR238J^{b)}</u>	<u>Al powder^{b)}</u>
25	1.0	0.5	0.6	--	0.5	5
26	1.0	0.5	--	0.6	0.5	5

a) Parts by mol.

b) Weight %.

Both resins, after cure, were tough (the BMJ (900) resin somewhat tougher), and adhered very well to 7075 aluminum, as well as to polyurethane-painted 7075 aluminum. From this point on, most screening tests were run on polyurethane-painted 7075 aluminum surfaces. Preliminary results of immersion in water are shown below:

<u>Resin No.</u>	<u>Volume Swell (%) in H₂O</u>	
	<u>24 Hr.</u>	<u>48 Hr.</u>
25	10	15
26	10	15

As can be seen, the aluminum powder and optimum cure seem to benefit both types of resins. These admittedly preliminary results are significantly lower in value than these of neat resin swelling tests as seen in previous work (27% and 35% in 24 and 48 hours, respectively --see Reference 1).

Task II (in part) - Hot Melt Tool Development

At this point work was initiated on the other main activity of Task II: Hot Melt Tool Development. This activity involved combining a commercially available hot-melt applicator, or modification thereof, with an ideally compounded and modified resin to form a convenient sealant/applicator system intended for quick-fix field repair. In a TRW survey of available applicators, those offered by the Hysol Division of the Dexter Corporation were found to be most appropriate for this application. (Indeed, the present-day applicators offered by Dexter/Hysol are adopted from TRW's model 100 applicator developed years ago).

In the previous program (NG2269-81-C-0738), the applicators studied were the Hipermatic TE and Hi-flo B models, a mechanically- and pneumatically-powered gun, respectively. They have been replaced by the Hipermatic 3000 and 4000 models. The model 4000 tool is especially promising because of a new modification: this pneumatically-powered gun has a Teflon-lined chamber to ensure easy passage of resin through the hot zone of the tool. For Task II, the Dexter/Hysol model 4000 tool was selected for further studies.

Slugs were cast of resins 25 and 26, and extruded through a Dexter/Hysol Model 4000 tool with a modified nozzle-tip in which the spring-and-ball mechanism was removed, so there was a clear, open path for resin to come through. The temperature of the "hot" zone was set at 204°C (400°F); the extruded resins 25 and 26 were voidy, spongy, and very difficult to move through the 1/8" diameter tip. What resin did come through, though, was at or near optimum cure, and did adhere to the polyurethane-painted aluminum surface.

This problem with elevated-temperature ($\geq 177^{\circ}\text{C}$ or 350°F) resin quality prompted experiments to determine possible causes along the lines of the speculations noted previously. In particular, this effort involved degassing the prepared resin to eliminate entrapped air as a possible cause of voids.

Attempts were also made to decrease the melt-flow viscosities of resins containing 1.0.0.5.0.6 MDA, BMPM, BMJ (900), and of MDA:BMPM:BMJ (D400-D2000), at elevated temperatures. These attempts consisted of increasing the concentration of the Kenrich KR238J titanate additive, in hopes that

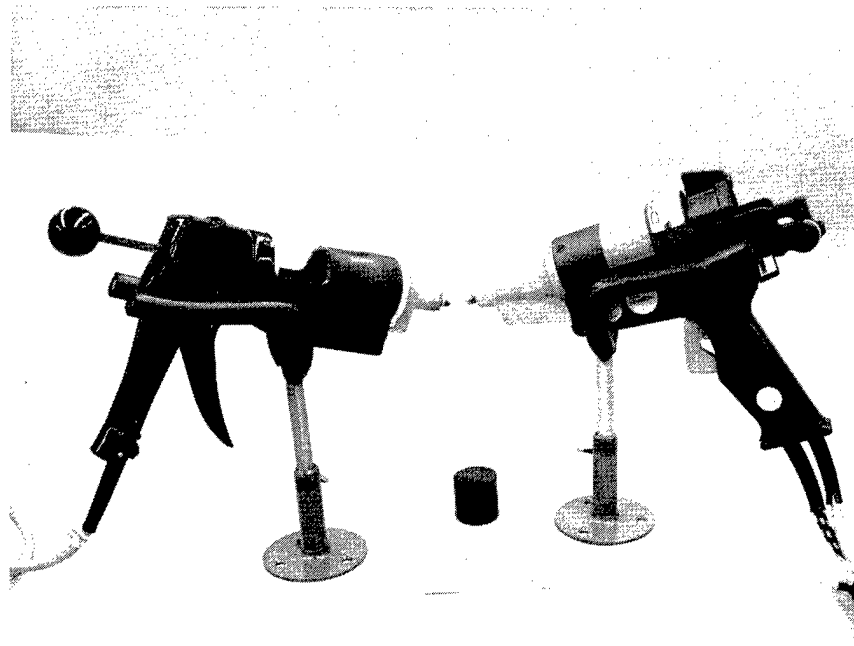


FIGURE 1. DEXTER/HYSOL HOT MELT APPLICATORS:
HIPERMATIC TE (LEFT) AND HI-FLO B (RIGHT).

Hipermatic te

(2)

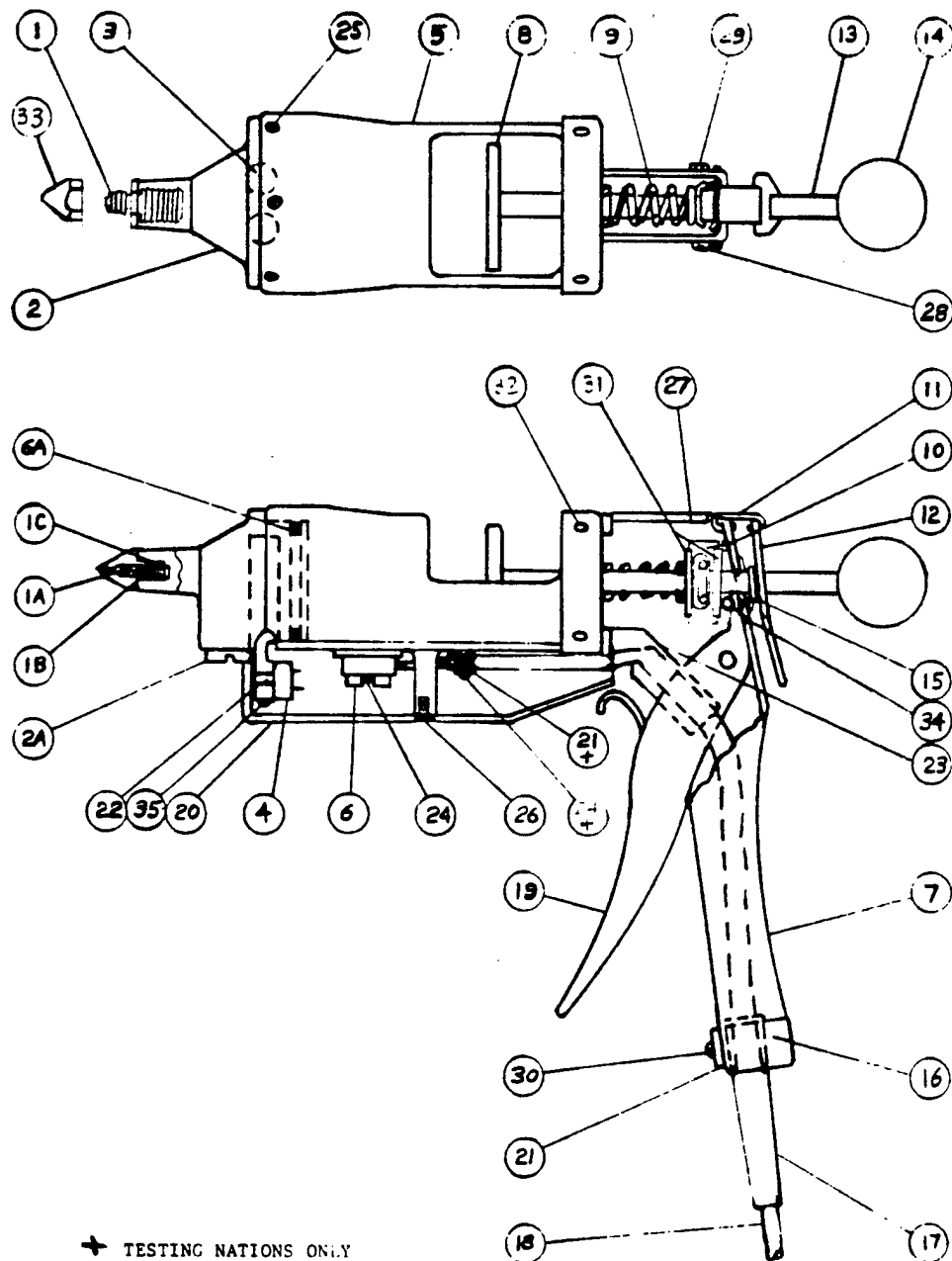


FIGURE 2. SCHEMATIC DIAGRAM OF DEXTER/HYSOL HIPERMATIC TE APPLICATOR

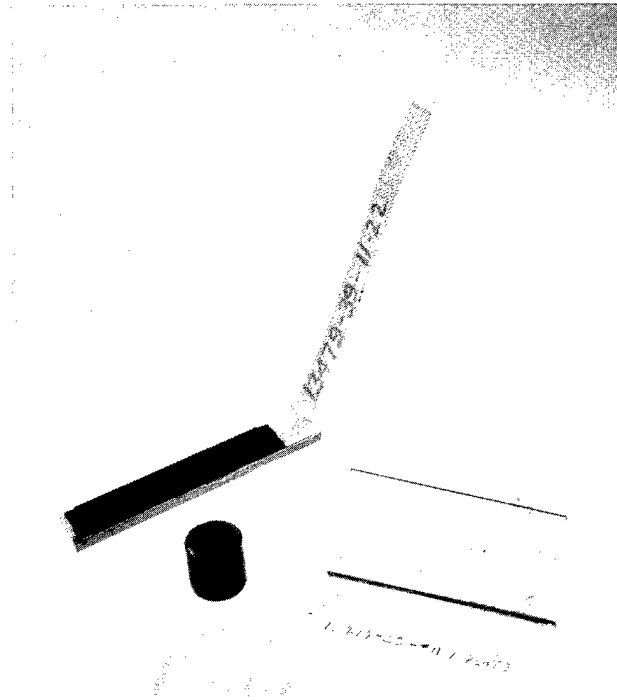


FIGURE 3. 180° PEEL TEST SPECIMEN, CAST SLUG, AND
FILLED-GAP TEST SPECIMENS.

adequate melt and flow would be possible at lower temperatures (300-350°F) than previously looked at, so the high-temperature-induced voidiness may be avoided. In addition, efforts were made to determine if the high-temperature-induced voids problem could be traced by differential scanning calorimetry (DSC) of monomer or polymer.

A sample of resin formulation 25 was prepared as described earlier, then cast into slug form and degassed in vacuo ($P \leq 1\text{mm}$) while cooling to room temperature. The material did indeed appear to lose some entrapped air during this treatment. Upon extrusion at 204°C (400°F), however, the same voids and sponginess problem was present. The implication, then, is that entrapped air is not the problem. Attention was then turned toward the possible, presence of volatiles by the proposed mechanisms a) and/or b) and d) noted on page 17.

Differential scanning calorimetry (DSC) was conducted on monomers and derived polymers. Some results are shown in Figures 4 - 8. MDA and BMPM showed sharp endotherms at 92.5°C (224°F) and 158°C (342°F), respectively. BMPM also showed a broad exotherm centered at 209°C (434°F), probably due to polymerization through the imide double bonds, and a slight broad endotherm centered at 120°C (274°F), most likely due to trace impurities rather than volatiles. The third key monomer, BMJ (900), showed the DSC scan shown in Figure 4. If volatiles are present, they could be evidenced by the endotherms from 120-160°C. This, however, is not easily interpretable since it is masked by the occurrence of the maleimide double-bond-type polymerization reaction. That is, the onset of this latter process obscures any evidence of volatile "outgassing", as shown by DSC scans of freshly prepared BMJ (900) and re-scanning of the already-scanned BMJ (900) sample. Nevertheless, the consequence of this avenue of investigation is that prepared BMJ (900) is "degassed" of trace volatiles by heating material at ca. 100°C for 8-12 hour prior to further use.

Whether this is sufficient to produce volatile-free resin in the reaction sequence of Equation 1 was investigated by the following experiments involving further DSC experiments. Typical resins prepared from this BMJ

Sample: #14301-83, BMJ(900)
 Size: 8.7MG
 Rate: 10C/MIN
 Program: Interactive DSC V2.0
 Date: 26-Jul-83 Time: 14:42:32
 File: 14301-83.01 T.A.#7
 Operator: TM
 Plotted: 26-Jul-83 10:05:51

DSC

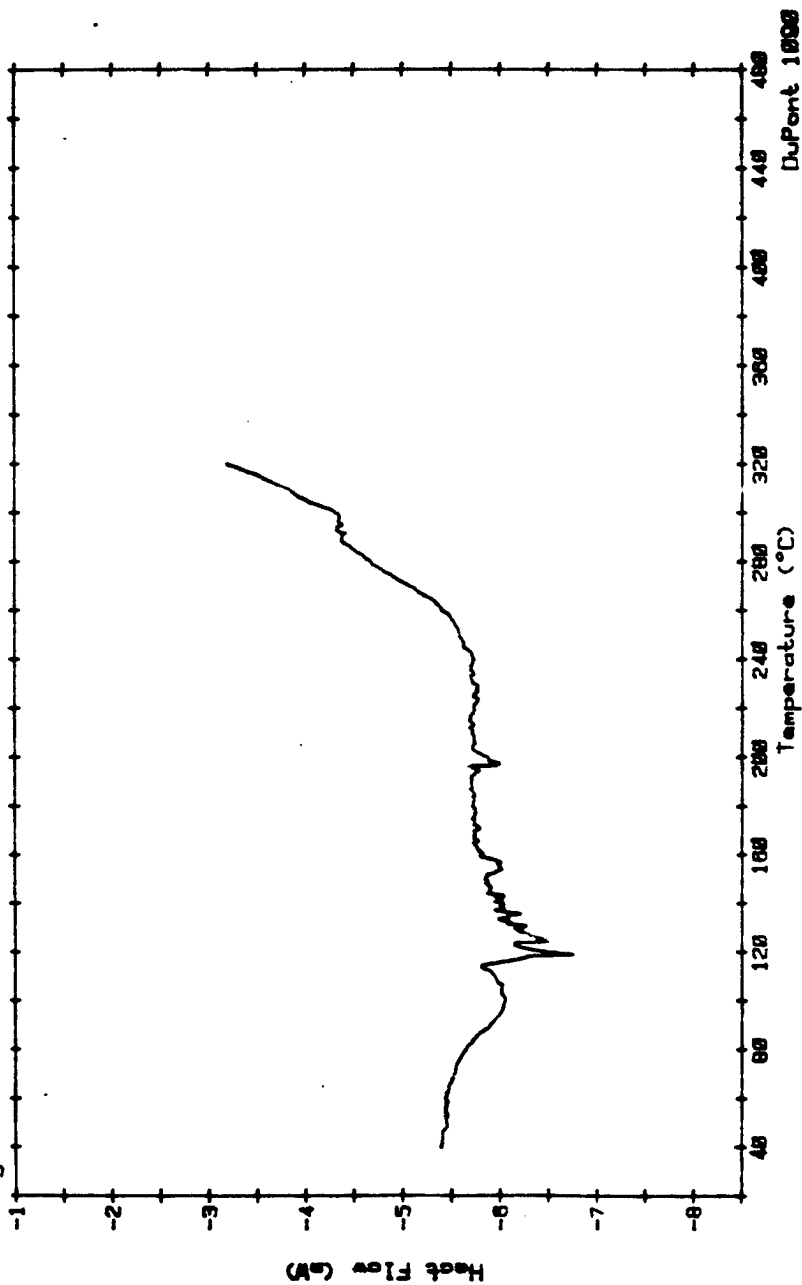


Figure 4. DSC Scan of BMJ(900).

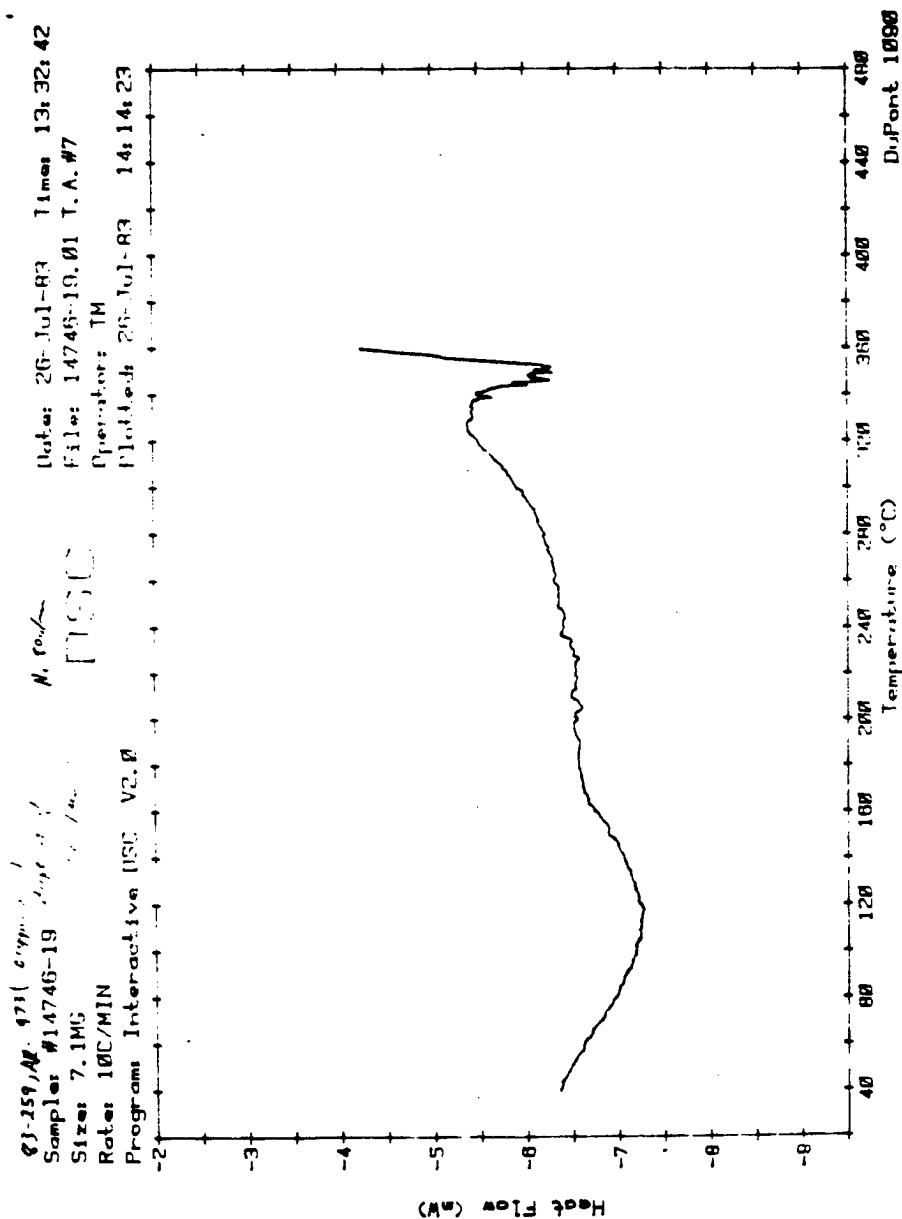


Figure 5. DSC Scan of 1.0:0.5:0.6 MDA:BMPM:BMJ(900) resin with 0.5 weight % KR238J and 4 weight % aluminum powder (#14746-19).

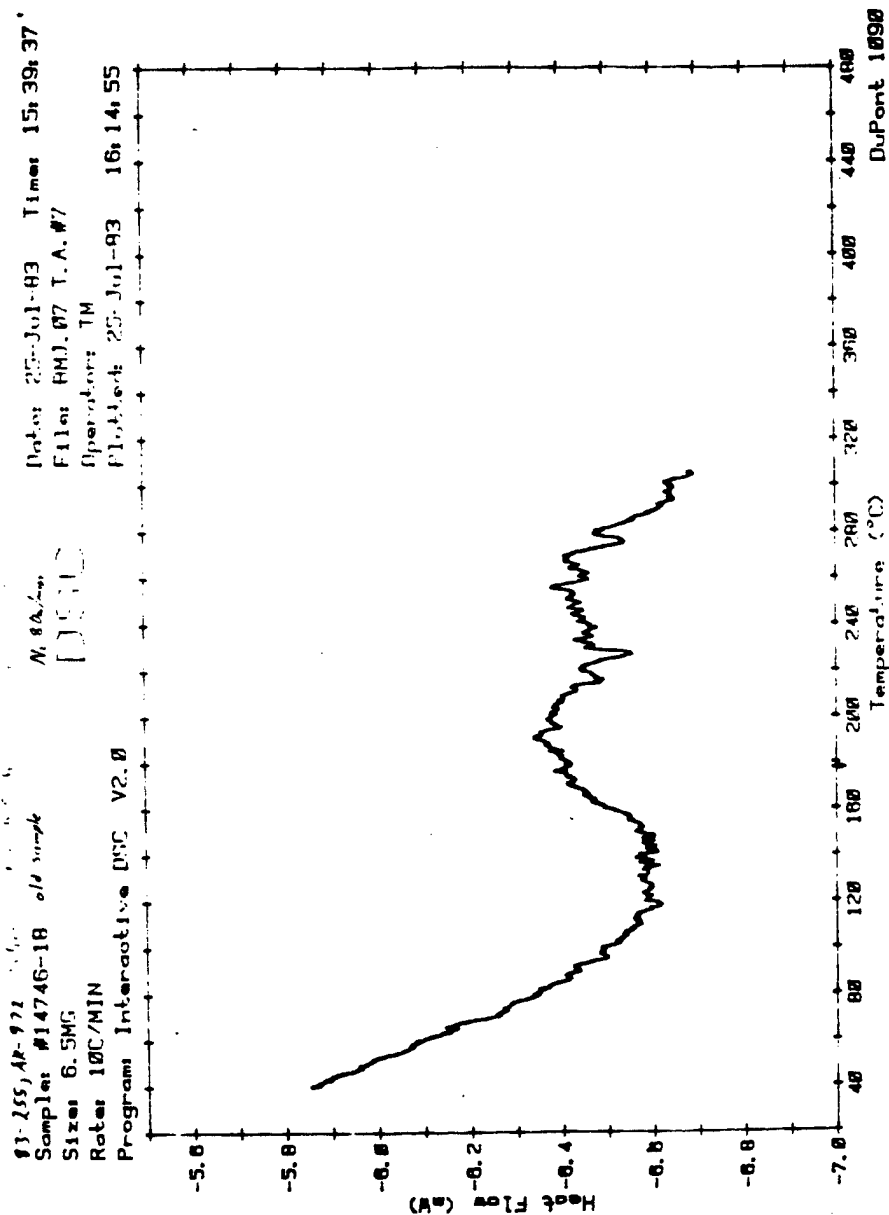


Figure 6. DSC Scan of 1.0:0.5:0.6 MDA:BMPM:BMJ(900) resin with 0.5 weight % KR 238J(#14746-18).

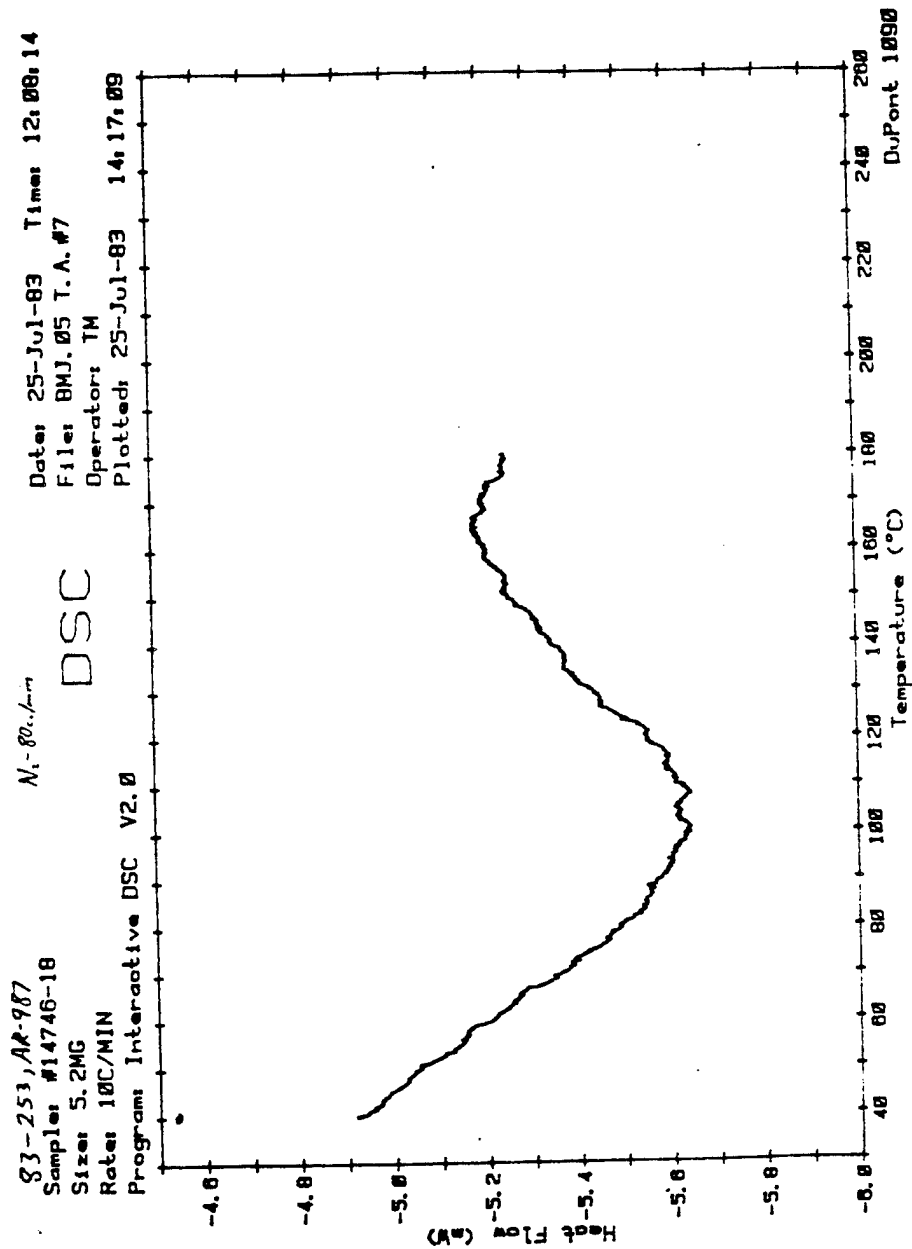


Figure 7. DSC Scan of #14746-18 (no prior heating).

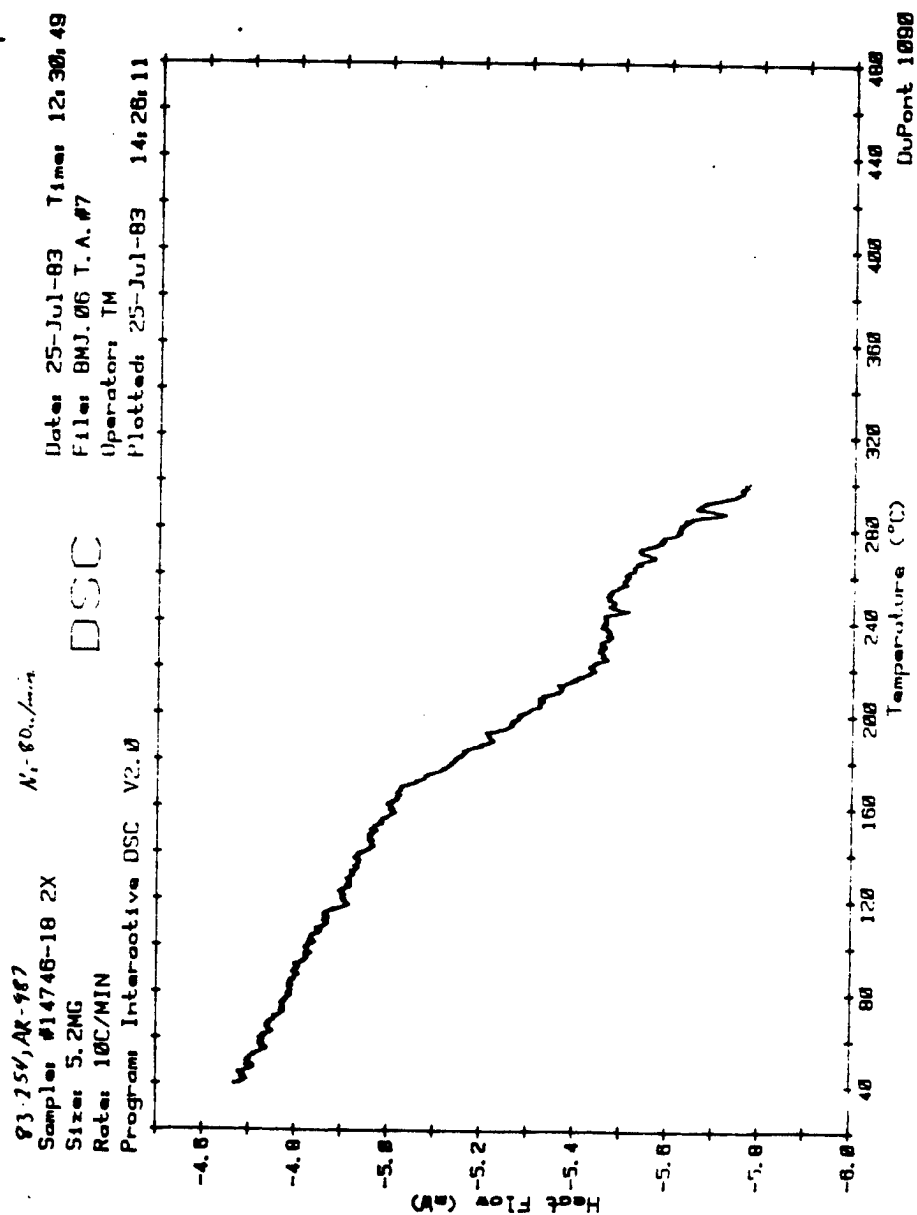


Figure 8. DSC Scan of #14746-18 heated to 190°C.

(900) (Figures 5 - 8) show no real evidence of volatiles; if they do exist, any evidence in these latter scans are masked by whatever else is going on with the resin (presumably a melting-type behavior with increasing temperature). An attempt to determine the cured resin's, as opposed to uncured resin's, behavior is depicted in Figures 7 and 8, where uncured resin was "scanned" to 180°C (382°F)--Figure 7--cooled, then re-run in the thermal analyzer to give Figure 8. No real conclusion could be drawn from these data. The only firm result is that any source of volatiles would be the synthesized BMJ (900). However, low-pressure devolatilization at elevated temperatures, as described above, would seem to obviate this as a cause for voids in derived resin.

At this time, it was deemed advisable, with concurrence of the NADC technical monitor, to conduct parallel immersion tests on a best-case commercially available hot-melt sealant along with TRW's modified hot-melt flexible polyamide resins. The resin chosen, upon consultation with commercial suppliers, was a modified polyamide resin offered by Dexter/Hysol (Pittsburg, California) known by its commercial designation of Dexter/Hysol 9001 resin. Though this material does not adhere very well to uncleaned aluminum surfaces, it does adhere well to chromate-converted and polyurethane-painted aluminum. When immersed in water, samples of the 9001 resin on aluminum showed little swell; however, at room temperature the clear amber material becomes opaque and slightly softer after 48 hours (Shore A hardness decreasing from 63 to about 60), while it becomes considerably softer at 60°C (140°F) in that same period of time (Shore A hardness decreasing from 63 to 38-40). In dilute MIL-C-43616 cleaning solution (9:1 v:v water:MIL-C-43616), the changes are even more dramatic; at room temperature, the Shore A hardness drops from 63 to 25 in 24 hours, while at 60°C (140°F), it becomes too soft to measure.

Immersion tests were run on 1.0:0.5:0.6 MDA:BMPM:BMJ (900) resin containing 0.5 weight % KR2385 titanate additive and 4 weight % aluminum powder, laid up on MIL-C-83286 topcoated 7075 aluminum and cured at 250°F for 4 hours (resin No. 27) in parallel with those on Dexter/Hysol 9001 modified polyamide resin on similar substrates. Volume swell and Shore A hardness data are shown below.

<u>H₂O Immersion at R.T.</u>								
<u>Resin</u>	<u>Volume Swell(%)</u>				<u>Shore A</u>			
	<u>0 Days</u>	<u>1 Day</u>	<u>2 Days</u>	<u>6 Days</u>	<u>0 Days</u>	<u>1 Day</u>	<u>2 Days</u>	<u>6 Days</u>
Flexible polyimide Resin #27	--	35	(16) ^{a)}	62	87	--	(87) ^{a)}	87
Dexter/Hysol 9001	--	2.3	(0) ^{a)}	12.3	63	--	(60) ^{a)}	60

a) Measured after 24-hr dryout.

<u>H₂O Immersion at 140°F</u>								
<u>Resin</u>	<u>Volume Swell(%)</u>				<u>Shore A</u>			
	<u>0 Days</u>	<u>1 Day</u>	<u>2 Days</u>	<u>6 Days</u>	<u>0 Days</u>	<u>1 Day</u>	<u>2 Days</u>	<u>6 Days</u>
Flexible Polyimide #27	--	30	(8.8) ^{a), b)}	41	87	87	88	88
Dexter/Hysol 9001	--	7.1	(1) ^{a)}	5	63	38-40	(37) ^{a)}	35

a) Measured after 24-hour dryout.

b) Topcoat peeled off aluminum; resin still adheres tenaciously to topcoat.

<u>Dilute MIL-C-43616 Immersion At R.T.</u>								
<u>Resin</u>	<u>Volume Swell(%)</u>				<u>Shore A</u>			
	<u>0 Days</u>	<u>1 Day</u>	<u>2 Days</u>	<u>6 Days</u>	<u>0 Days</u>	<u>1 Day</u>	<u>2 Days</u>	<u>6 Days</u>
Flexible polyimide #27	--	36.2	(11.1) ^{a)}	36	87	87	(87) ^{a)}	87
Dexter/Hysol 9001	--	9.2	(6.2) ^{a)}	16.2	63	22-27	(40) ^{a)}	-- ^{b)}

a) Measured after 24-hr R.T. dryout.

b) Too soft to measure.

Dilute MIL-C-43616 Immersion At 140°F

<u>Resin</u>	<u>Volume Swell (%)</u>				<u>Shore A</u>			
	<u>0 Day</u>	<u>1 Day</u>	<u>2 Days</u>	<u>6 Days</u>	<u>0 Day</u>	<u>1 Day</u>	<u>2 Days</u>	<u>6 Days</u>
Flexible polyimide #27	--	22 ^{a)}	--	37	87	84	--	87
Dexter/Hysol 9001	--	-- ^{b)}	--	--	63	--	--	--

a) Topcoat peeled off aluminum; resin still adheres tenaciously to topcoat.

b) Too soft to measure; test discontinued.

There is an apparent discrepancy between room temperature and 140°F water immersion data for the flexible polyamide resin as well as between water immersion and dilute MIL-C-43616 immersion data. This may be due to human error; more care taken in further tests though, did not completely verify or obviate this discrepancy.

If mechanism d) (see page 17) is operating--that is, a high-temperature reaction producing volatiles and subsequent voids--the most likely source would be the relatively labile tertiary hydrogens on the carbon atom bonded to the nitrogen derived from the Michael reaction of diamine and maleimide functionality. This is almost certainly a free-radical process; to circumvent it, addition of an antioxidant was proposed and, with concurrence of the NADC technical monitor, investigated.

Several antioxidant candidates were investigated. Initially it was a hindered-phenol type material 2,6-di-tert-butyl-4-methylphenol (BHT), a commonly used antioxidant. Upon consultation with appropriate TRW representatives and various vendors experienced with the additive, preliminary studies with BHT additive were conducted, with the optimum formulation as evidenced by extrudability balanced against adhesion and toughness characteristics. This formulation was a BMJ (900)-containing baseline resin containing 1% (w/w) KR238J additive and 0.2% (w/w) BHT, with extrusion through the Dexter/Hysol applicator at 177C (350°F). The result was better flow and significantly lower void content as applied through the chosen applicator. The resin adhered quite well to Alodine-converted 7075 aluminum, but did not survive room temperature immersion in either water or dilute MIL-C-43616 past 24 hours. This result implies insufficient cure,

and points toward the use of high-temperature (e.g., 350°F and above) cure promoter additives as a possible method to attain maximum cure upon extrusion, as described below.

Attempts to optimize hot-melt application/cure properties of modified baseline resins in absence of cure promoters (as described on page 19 of this report) by varying concentrations of KR238J additive showed that there is indeed an optimum concentration of this rheology-modification material, specifically between 0.5-1% by weight of total resin/additive content. The fact that higher concentrations (2% and above) do not aid hot-melt applicability--and, in fact, do hamper it--verifies the advice and evidence of various consultants,² and suppliers of these materials. This avenue of investigation was then quickly abandoned in favor of balancing the antioxidant/rheology control/- high-temperature cure-promoter formulation efforts as mentioned above.

Also, in this particular time frame, efforts to optimize rheology - control-agent (i.e., KR238J)/antioxidant (i.e., BHT) resin compounding efforts with the BMJ (D400-D2000) mixtures met with little success. These resins are significantly more resistant to water and dilute MIL-C-43616 cleaning solution immersion than their corresponding BMJ (900)-derived counterparts; however, they are not nearly as tough, resilient, or adhesively strong as those latter resins, even under various long-term cure, compounding, filler/property correlation conditions (by as simple means as manual exam). Though this seems a non-viable pathway to pursue toward achievement of this program's goals, the solvent/immersion properties may nevertheless point a way toward an optimization effort.

At this stage of the program, however, it became readily apparent that the unique objectives of this work necessitated recommendation for further resin modification, compounding, and evaluation.

In light of previous work, this further effort concentrated on achieving a satisfactory balance among rheology control/cure promoter/antioxidant concentrations for the purpose of developing a suitable hot-melt flexible polyamide sealant candidate for quick-fix field repair of Naval aircraft. For this purpose, various concentrations of the aforementioned additives were investigated in conjunction with baseline resin for adhesion/environmental behavior properties.

Initial efforts involved the compounded formulations shown below. Compounded resins were all extruded through the Dexter/Hysol 4000 modified hot-melt applicator tool (see page 19) at 177°C (350°F), 204°C (400°F), and 232°C (450°F).

Formulary Ingredient (percent by weight)

Resin # ^{a)}	KR238J	Aluminum	BHT	Irganox 1098	Lupersol 101	Di-Cup R	Ammonium Chloride
28	1	4 ^{b)}	--	--	--	--	--
29	1	4 ^{b)}	0.4	--	--	--	--
30	1	4 ^{b)}	--	--	1	--	--
31	1	4 ^{b)}	--	0.8	1	--	--
32	1	4 ^{b)}	--	--	--	1	--
33	1	4 ^{b)}	--	1	--	1	--
34	1	4 ^{c)}	--	1.7	--	--	1

a) Baseline resin is 1.0:0.5:0.6 MDA:BMPM:BMJ(900) 1.0:0.5:0.6, parts by mol.

b) Fine brilliant aluminum powder.

c) Atomized aluminum powder.

BHT is 2,6-di-tert-butyl-4-methylphenol, a common antioxidant. Irganox 1098 is a recommended antioxidant available from Ciba-Geigy. Lupersol 101 (available from Pennwalt) is a common organic peroxide cure promoter, 2,5-di-tert-butylperoxy-2,5-dimethylhexane. Di-Cup-R is another peroxide cure promoter, dicumyl peroxide.

Those formulations employing peroxides as cure promoters still showed some voids content upon extrusion and difficulty in the extrusion process itself. The most likely cause may be that peroxides initiate a high-temperature radical process which evolves volatiles, despite the presence of antioxidant. To circumvent this, a weak acid, ammonium chloride, was used as initiator, since the crosslinking process can be acid-catalyzed as well. A higher concentration of Irganox 1098 and a different type of aluminum powder, more dense than previously used, were the other changes made. The ensuing resin, No. 34, was much more easily extrudable through the tool under similar conditions and was almost totally free of voids. In addition, it adhered quite well to both Alodine-converted and topcoat-painted 7075 aluminum. The one slight drawback is that it is not at optimum cure immediately upon extrusion; this may be remedied by greater amounts of acid catalyst (either ammonium chloride or another acid of similar strength).

Further contact with representatives from Kenrich Petrochemicals, Inc., elicited a suggestion to use a new proprietary product, KR 5544, as an adhesion promoter as well as viscosity improver, in place of the KR238J used previously. The KR5544 is another organic titanate which is supposedly stable at high temperature (up to 900°F) and has been shown to increase adhesive properties of some polyimide materials. A sample was forwarded to us and employed in the preparation of some flexible polyimides; in our systems, the KR5544 imparted little or no decrease in viscosity as opposed to resin prepared without titanate additive. For this reason, it was decided to go back to using KR238J as an additive to decrease resin viscosity.

Some effort was made to investigate the effect of different acids as cure promoters in the resin. Specifically, oxalic acid was employed as a cure promoter. An additional effort to re-investigate the effect of a water-resistant silica filler, Aerosil R972, on the resin's water resistance was also made. The formulations studied are listed below.

Formulary Ingredient (percent by weight)

<u>Resin</u>	<u>KR238J</u>	<u>Aluminum</u>	<u>Irganox 1098</u>	<u>Oxalic Acid</u>	<u>Aerosil R972</u>
35	1	5	3	2.4	--
36	1	4	3	2.4	2.0
37	1	5	3	2.4	2.5

All three formulations extruded easily through the Hysol 4000 hot-melt applicator and adhered fairly well to Alodine-treated 7075 aluminum substrate. However, it was evident that only partial cure of these resins was effected. It is possible that extrusion at 450°F, or perhaps higher levels of oxalic acid or similar acid cure promoter, could give optimum or near-optimum cure upon extrusion. For this reason, the hot-melt applicator extrusion studies from this point on were conducted at an extrusion temperature of 232°C (450°F).

Studies on compounding ingredients then narrowed down to balancing aluminum powder and Aerosil R972 additives for viscosity control, and Irganox 1098 antioxidant and organic acid cure catalysts for optimum extrusion/cure properties. An optimum blend of 8% w/w aluminum powder and 5% Aerosil R972 gave a resin that showed satisfactory dimensional stability at room temperature when cast into slug form, i.e., there was no slump or cold-flow. Any substantially greater amount of these thixotropic agents made the resultant resin too viscous to handle at the final reaction temperature of ca. 100°C, even with the now-commonly-employed 0.5-1% w/w KR238J titanate additive present. With rheology control thus fixed, attention was focused on antioxidant/cure catalyst concentrations.

The presence of antioxidant lends compounded resin a low enough melt-flow viscosity at the 232°C applicator temperature to extrude a representative slug (ca. 45-gram mass) without any noticeable "overcure" or clogging of resin in the applicator. What results is a smooth void-free bead of resin that adheres very well to 7075 aluminum, both Alodine-treated and coated with the usual MIL-C-83286 topcoat. A sufficient concentration of antioxidant seems to be about 4% (w/w) of total resin content; this then became a standard amount used in subsequent resins. The drawback is, again,

insufficient cure in the extruded resin. The effort then was directed toward acid curing agent concentration studies to achieve this goal properly.

Initial success was seen with varying amounts of oxalic acid: 2-4% (w/w) gave extruded resin of significantly tougher quality than those without. There is an optimum concentration: above 4% by weight, extruded resin had considerable voids and apparent "overcure", leading to extrusion difficulties and plugging of the Dexter/Hysol hot-melt applicator. Other organic acids were investigated to hopefully avoid this complication--in particular benzoic acid and several other aromatic-type candidates (e.g., phthalic and terephthalic acids). None of these proved as satisfactory as oxalic acid at 4% w/w concentration in imparting comparable toughness to extrude resin while maintaining adhesion and void-free characteristics.

Of these investigations with rheology-control titanate additive, thixotropic agents (aluminum and Aerosil R972), antioxidant (Irganox 1098), and acid cure catalyst (oxalic acid), the most promising resin in terms of extrudability, adhesion, initial toughness and flexibility is then this formulation:

<u>Resin^{a)}</u>	<u>Compounding ingredient^{b)}</u>				
	<u>KR2385</u>	<u>Aluminum Powder</u>	<u>Aerosil R972</u>	<u>Irganox 1098</u>	<u>Oxalic Acid</u>
38	1.0	8	4	4	4

^{a)} Baseline resin is MDA:BMPM:BMJ(900), 1.0:0.5:0.6 parts by mol.

^{b)} Percent by weight.

Task III: Finalized Sealant Evaluation Studies

This task proposed to subject the most promising resin from Tasks I and II to various environmental exposures as peel adhesion test specimens. The specific tests were:

- (a) JRF or JP4, 7 days at room temperature
- (b) MIL-L-23699 oil, 7 days at room temperature
- (c) Oven aging, 7 days at 82°C (180°F)
- (d) Water/vapor, 7 days at 49°C (120°F)

Peel adhesion tests were to be conducted before, after 3 days, and at the conclusion of these exposure periods. Low-temperature flexibility and adhesion (to as low as -54°C, or -65°F) by an arc-bend technique was also to be tested before and after aging 3 days at 82°C (180°F) and after 3 continuous thermal shock cycles (82°C to -54°C). Storage stability was examined (melt viscosity, adhesion, water resistance, general water resistance and application properties) after accelerated storage (14 days at 49°C) and after ambient storage for one year.

Resin No. 38 was cast in slugs and extruded at 232°C onto Alodine-treated and also onto MIL-C-83286 topcoated 7075 aluminum panels. As mentioned previously, these sealant beads adhered very well to both substrates. Low-temperature flexibility was checked by immersion into a Dry-Ice-Isopropanol bath at -54°C; while the material did not lose adhesion, it did become brittle and actually cracked when bent in an arc past about 30 degrees. Samples run through thermal shock cycles similarly retained adhesion properties, but cracked due to embrittlement upon bending in a 30 degree arc. This is in marked contrast to neat baseline polymer, which show flexibility down to -54°C.

Further low-temperature studies revealed that ca. -30°C was a critical temperature for this compounded resin. At this temperature, the sealant bead did remain cohesively intact as well as adhered to substrate, although the resin did become considerably harder. This points toward further efforts to improve low-temperature properties (perhaps with a low-temperature plasticizer type of additive).

When stored at 49°C for 14 days, representative slugs were extruded at 232°C with similar case as slugs of freshly-prepared resin. Adhesion properties and absence of voids were similar by manual exam; therefore, this temperature and time duration present no complications for storage of resin slugs at this temperature.

Typical 180° peel-test specimens were prepared on Alodine-treated and MIL-C-83286 topcoated 7075 aluminum by the method of MIL-S-8802D. The resultant specimens showed values of peel strength, with cohesive failure, of comparable values to those of neat resin specimens--that is, 60-85 pli (see Final Report on N62269-81-C-0738). Again, there is scatter in obtained values; however, failure modes were cohesive in every case of several samples prepared.

These 180° peel-test specimens were prepared with resin extruded from the Dexter/Hysol applicator at 232°C. The resultant resin showed fairly low Shore A hardness values (ca. 30-35). Note that this is without any additional cure at medium temperatures (ca. 120°C) for 1-2 hours, which was seen to give Shore A hardnesses of 60 and higher. This implies, again, potentially insufficient cure of resin and consequent low resistance to fluids exposure, especially water or vapor at elevated temperatures.

Initial exposure testing unfortunately bore out this possibility. Since water resistance has always been emphasized as the key environmental property, samples of these peel test specimens were first placed in water at ambient temperature. Within 24 hours, resin had swelled (well over 100% by volume), softened to the point where Shore A measurements were impossible, and in most cases already debonded from aluminum substrate as well as the metal mesh screen. None survived long enough to obtain peel strengths after 3-day exposures.

An independent TRW-initiated effort, though, showed that samples of filled resin No. 38, when cured further at 130°C for two hours in an oven, showed increased Shore A hardness and higher resistance to water and humidity (lower volume swell and hardness decrease, little peel strength degradation), comparable to neat baseline resin properties as reported in the previous program. While preliminary and not ideally quantitative,

this little side-study emphasized that the compounded resin No. 38, if cured properly, may show promise to meet the goals of this program.

However, due to the necessary additional effort in compounding and resin formulation to bring resin/applicator development to this point, no further time or budget was available to allow renewed efforts in improving and/or modifying resin No. 38 in hopes of attaining satisfactory performance goals in these environmental exposure tests. Only preliminary results of exposure in jet fuel, oil, and in-oven and humidity aging were obtained. Peel test data were not obtained on aged samples; nor were definitive quantitative data on volume swell or Shore A hardness change obtained. General trends were that volume swell in fuels and oils of these extruded resins over at least 2-3 days was significantly higher than seen in longer-cured resins, both neat and compounded (>10% as opposed to 1-2% for the longer-cured samples as seen in previous and ancillary work). This points out the significance of proper cure conditions to ensure resin stability and resistance even in the hydrocarbon-based fluids.

At this time, however, the disappointing results with water resistance and the necessary curtailment of technical activity in this program have demonstrated that the efforts reported so far in this final report have not been sufficient to develop the hot-melt processable flexible polyimides as a hot-melt field-repair sealant candidate at this time.

Task IV. Field Demonstration. This task was intended to employ the most promising sealant/applicator system in an actual field demonstration of a sealing operation at a site selected by the NADC project engineer. While the sealant/applicator system developed so far does apply resin satisfactorily onto substrates and into systems needed to be sealed, the insufficient cure characteristics of freshly-extruded resin and consequent low resistance to environmental exposure have prompted the NADC project engineer to suggest foregoing this task in this program at this time. As a result of dialogues between TRW and NADC, Task IV, then, has been removed as a necessary step in performance of the statement of work, with concurrence of the NADC project engineer.

III. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The results of the work performed on Contract N62269-82-C-0732, as presented in Section II of this final report, demonstrate that the flexible polyimides studied herein can be modified, compounded and formulated to provide only a baseline hot-melt sealant/applicator system. Key properties of these modified flexible polyimides developed to date are:

- High adhesion to typical adherent surfaces.
- Significant toughness and flexibility after high-temperature extrusion (177-232°C).
- Sufficiently low melt-flow viscosity and long enough work time at 177-232°C to extrude with relative ease onto structures, void-free, highly adhesive sealants.
- High toughness and flexibility when sufficiently cured (120°C for 1-2 hours, or 177-232°C for 15-30 minutes).
- Increased resistance to fuel, oil, and hydrolytic conditions when sufficiently cured (120°C for 1-2 hours, or 177-232°C for 15-30 minutes).
- Elevated temperature (49°C) stability.
- Prepared from low- to medium-cost, commercially available starting materials.

The results also demonstrate that, while work on this program has developed a workable sealant/applicator system, the goal of developing a quick-curing (5 minutes or less) hot-melt resin with key performance properties (fuel and oil resistance, hydrolytic stability) immediately following extrusion has not been achieved. There are several areas requiring further work and optimization before a field-ready system employing the hot-melt processable flexible polyimides is available. These areas are described below:

- Hydrolytic stability of extruded resin must be improved. This could be accomplished by a) additional compounding changes including the base polymer crosslinking agents, fillers, etc; b) latent cure promoter additives which are activated by the elevated temperature of extrusion and continue to promote cure even after extrusion and at

lower temperatures; c) microencapsulation of cure promoters or crosslinking agents which are released at elevated temperatures and effect satisfactory cure. The use of an improved water-resistant polymer is probably the preferred method.

- Fluids stability of extruded resin must be improved. The achievement of further cure by any of the methods above would most certainly impart this to the resin.
- The cure/fluid resistance properties must not affect the elevated-temperature melt-flow viscosity and work time so that hot-melt extrusion will be relatively easy; nor must they affect the adhesion properties already achieved (high adhesion to typical substrates, cohesive failure in peel).
- Low temperature flexibility of compounded resins must be improved, possibly by inclusion of plasticizers in the compounded formulation.

These compounded and filled flexible polyimide resins have been shown to possess considerably higher performance properties than the neat resin formulations developed by TRW before, namely higher adhesion and toughness characteristics, as well as reproducible ease and efficacy in extrusion through a hot-melt applicator with only minor modifications. While the goals of this program have not been fully achieved, the efforts have focused attention on the areas for improvement, namely sufficient cure upon extrusion to give fluids resistance without increasing elevated-temperature melt-flow viscosity and decreasing work time. (Should the latter be a problem, development of a disposable-dosage type of hot-melt applicator, with a removable capsule/heater-tip arrangement, may be a solution to prevent potential "overcure" and clogging of the applicator. This would be a considerably more ambitious applicator development task than considered up to now). Perhaps more important is the need to improve the resistance of the baseline polymer to water and other fluids. An improved water-resistant polyimide that retains the elevated-temperature flexibility and work-time in an appropriate applicator, as well as

incorporating an effective latent-curing mechanism in reasonable post-application time periods (minutes), needs to be developed or made available before the promise of this resin system as a viable candidate for a quick-curing field-repair sealant can be fulfilled.

REFERENCES

1. Chang, G. E. C., Development of Hot Melt Flexible Polyimide Sealants for Rapid Sealing of Aircraft and Missiles, Final Technical Report, NADC Contract N62269-81-C-0738.
2. Titanate Coupling Agents for Filled Polymers, Ken-React Reference Manual, Bulletin No. KR-0278-7, Revision #2, Kenrich Petrochemicals, Inc., Bayonne, N.J. 07002.